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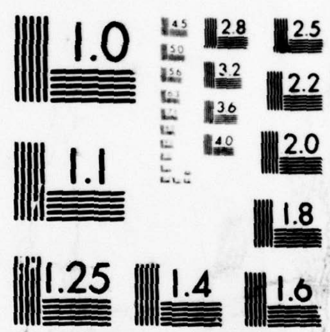

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Final Report

Ferroelectric Polymers

by

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June 1, 1979

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Polybenzimidazoles were studied as potential ferroelectric polymers after a model, 2-ethylbenzimidazole, was shown to be ferroelectric. Three polymers were studied as the formate salts. They were interesting and showed large polarization, but were not pyroelectric or ferroelectric. One polymer may be antiferroelectric with $T_{(c)} = 40°C$. Nylon 11 was shown to be polable and was then pyroelectric.

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Ferroelectric Polymers

by

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The major thrust of this work was to find ferroelectric polymers. We were not successful, though one lead remains to be studied.

The work done under contract N00014-67-A-0404-0011 broke down as follows.

I. Equipment Building

We built several versions of a temperature controlled dielectric cell which could also be used for poling and measuring pyroelectric currents. The final version, used presently, was built under an ARO-D contract.

In cooperation with the Electrical Engineering Department, we built an automatic dielectrometer which scanned at 50, 500, 5K and 50K Hz. Part of the salary for two people who helped build the instrument came from this grant. It is now being used very effectively by several groups in the Department. At the time it was built, there were no such instruments on the market.

II. Small Molecule Studies

Using recrystallized material, we established the ferroelectric nature of 2-ethyl benzimidazole. We also determined the crystal structure of the material at room temperature (not published). This made us believe that polybenzimidazoles were worthwhile studying as they might show interesting electrical properties.

III. Polybenzimidazole Studies

Three polymers in the 2,2'-bibenzimidazole series were made, those with $-(CH_2)_4-$, $-(CH_2)_8-$ and $-(CH_2)_{12}$ connecting links. We were interested in crystalline materials and initial work showed that the neutral polymers were amorphous. We then worked with the formic acid adducts-films cast from formic acid which were crystalline and stable. The $-(CH_2)_8-$ sample showed unusual electrical behavior, with a large rise in ε' and ε'', reaching a maximum at 120°C, ε' at 50 Hz $\approx$ 1200, where the crystalline form decomposed. After long consideration we decided that, as the formic acid complex was in the salt form and thus symmetrical, the behavior could not be due to ferroelectricity but was probably due to interfacial polarization which disappeared in melting. The crystal structure of the formate complex of the $(CH_2)_8$ bibenzimidazole was determined and will be published.

We then studied the neutral polybenzimidazoles. Only one could be crystallized. This was the tetramethylene derivative. Here the dielectric constant and tan δ showed a sudden frequency independent drop at -40 to -50°C, which suggests an antiferroelectric transition (see Fig. 1.). We hope to follow this up in the near future.

IV. Other Polymers

As we were convinced that odd Nylons also should be electrically active, we studied Nylon 11 and found that it could be poled. It showed reasonable pyroelectric activity-about the same as PVF_2 poled under similar conditions (about 10% of present PVF_2 activity). However, it showed very little piezoelectric activity, for reasons which are not yet understood.

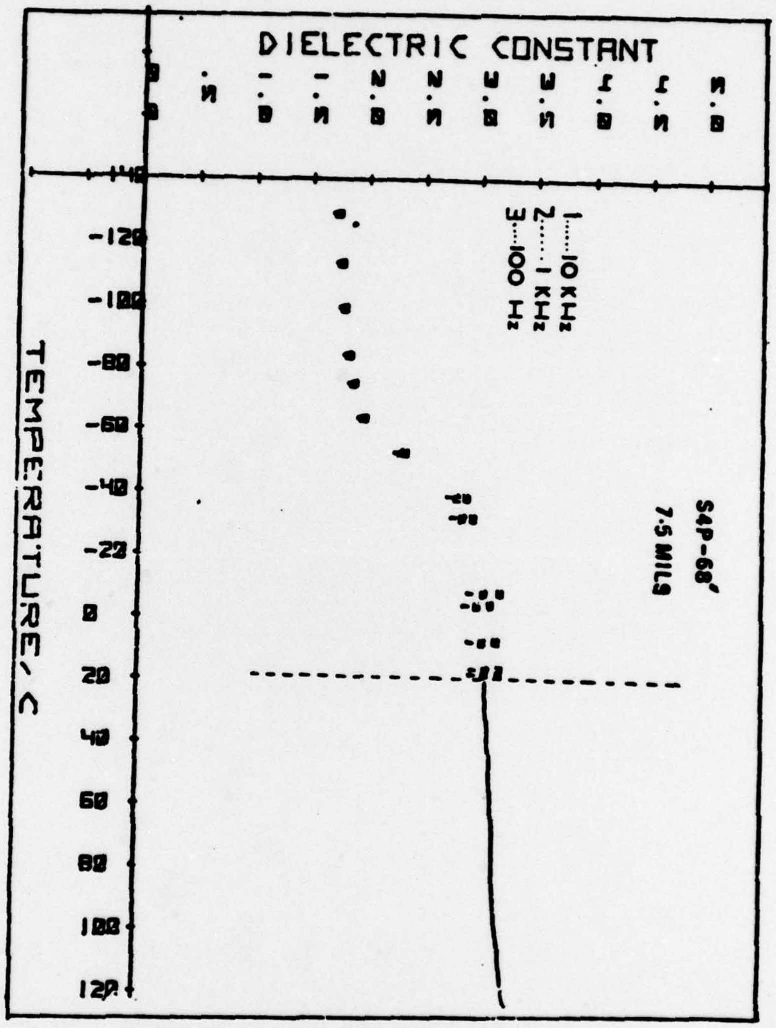

Figure 1 (a). Poly(tetramethylene bibenzimidazole) (S4P-68"): dielectric constant versus temperature; portion of plot to right of dotted line represents data obtained with an Audrey II continuous scanning dielectrometer at 1 KHz.

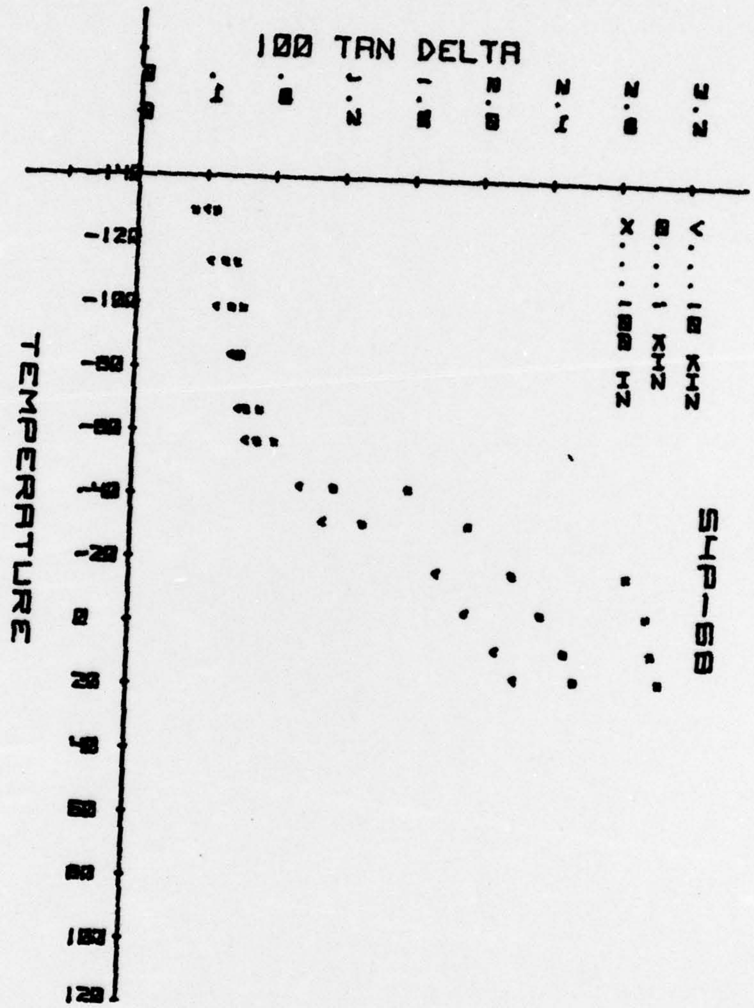

Figure 1.(b). Poly(tetramethylene bibenzimidazole) (S4P-68"): tanδ versus temperature.

Scanning for Ferroelectricity in Polycrystalline Materials

by

M. Litt, Che-hsiung Hsu, P. Basu and S. M. Aharoni
J. Appl. Phys., 46, 3250 (1975).

The dielectric behavior of polycrystalline pellets of 2-alkyl benzimidazoles are reported in this paper. The experimental technique consists of measuring the dielectric constant of a polycrystalline pellet as a function of temperature. Dielectric anomalies were found for which the position of the dielectric and loss-tangent peaks were independent of frequency, which showed a solid/solid first-order transition. When the sample dropped through the transition temperature, reversible charge storage showed poling of the sample, and therefore implies possible ferroelectric behavior. The experimental procedure was validated on thiourea, a known ferroelectric. 2-ethyl benzimidazole showed the same phenomena at a transition temperature of about -90°C and is probably a new ferroelectric material.

Pyroelectricity and Piezoelectricity in Nylon 11

by

Morton H. Litt, Che-hsiung Hsu and P. Basu
J. Appl. Phys., 48, 2208 (1977).

This paper describes preliminary pyroelectric and piezoelectric results obtained with commercial films of Nylon 11. The results of dielectric-constant measurements in the temperature range 20-130°C are also presented. Nylon 11 films show quite high pyroelectricity and the evidence indicates that there is probably dipole orientation in crystalline regions. Charge injection or volume polarization, as well as dipole orientation, was shown to contribute to the pyroelectricity unless the sample was thoroughly relaxed.

Thesis: Synthesis and Characterization of Poly(Polymethylene Bibenzimidazole) Polymers and Model Compounds

by

Pijus K. Basu

Three polymers of the poly-2,2'-(polymethylene)-5,5'-bibenzimidazole family (the tetra-, octa-, and the dodecamethylene homologues) were synthesized with the objective of examining their electrical properties, particularly those that could be related to possible ferroelectric-paraelectric transitions in these materials.

As part of the general characterization of these polymers, several of their non-electrical properties were also studied. Most of the characterization was done on cast films of the polymers. All the polymers dissolved in formic acid and were cast into films from this solvent. These films were crystalline in most cases and contained formic acid even after vacuum drying; the major part of this work describes the results obtained with these formic acid-cast films. The characteristics of the formic acid-cast films examined included: formic acid content, mechanical properties, crystallinity, thermal transitions, water absorption, IR absorption, and the effects of temperature on some of these preceding properties. Similar properties were also studied for a few films cast from the neutral solvents dimethyl formamide and dimethyl acetamide.

Of the three polymers, most attention was paid to the octamethylene homologue. The formic acid-cast film of this polymer was crystalline and showed polymorphism--three different crystal structures were identified.

Highly oriented films of the octamethylene polymer were obtained and these contained very small amounts of formic acid. They also gave very good fiber patterns. Thermal transitions, corresponding to the melting of the crystalline structure, were seen in both oriented and unoriented samples. This polymer did not form crystalline films from neutral solvents. The other two polymers showed generally similar behavior, except that no thermal transition corresponding to the melting of the crystalline phase was seen in the tetramethylene polymer. This polymer also was the only one to form a neutral, crystalline film (from dimethyl formamide).

A major effort was the attempt to solve the crystal structure of the room-temperature modification of the formic acid-cast film of the octamethylene polymer. This posed several problems due to the limited data, and variability in formic acid content. The unit cell obtained had the following dimensions: $a = 5.17Å$, $b = 10.11Å$, $c = 20.47Å$, $\alpha = 81.85°$, $\beta = 67.12°$ and $\gamma = 59.41°$. There were two chains per unit cell and three to four formic acid groups. A structure was obtained that satisfied stereochemical requirements and also agreed fairly well with the x-ray intensity data. The positions of the formic acid molecules could not be exactly defined but indications were obtained as to their general locations in the unit cell.

For all the polymer films, the variation of the dielectric constant and the loss factor as a function of temperature were studied. For some of the films, more detailed investigations were made regarding the frequency response behavior, conductivity, and the possibility of inducing pyro- and piezoelectric properties. The results show that, for the formic acid-cast films, the dominating factor is the high D.C. conductivity, which leads to interfacial polarization. This causes very high values of the measured dielectric constant and stored charge. The neutral, crystalline film of the tetramethylene polymer showed a transition at -50°C in the dielectric constant and loss factor; this may be an antiferroelectric transition.

Polymers with Unusual Electrical Properties

by

M. Litt, Che-hsiung Hsu, P. Basu and T. Noveske
Proceedings of Piezoelectric and Pyroelectric Symposium Workshop, NBSIR 75-760, M. G. Broadhurst, Coordinator.

Poly(octamethylene dibenzimidazole) is an amorphous polymer. When cast from formic acid, crystalline films of the 1:1 complex of benzimidazole/formic acid are obtained. The crystalline polymer shows large peaks in the dielectric constant and loss factor at 120°C which are frequency independent, indicating a first order process. The value of the dielectric constant at the top of the peak is about comparable to values obtained for single crystals of ferroelectric substances. Such films also store large amounts of charge on being poled, and exhibit spontaneous current flow and voltage. The variation of the magnitudes of the current, charge, and voltage as a function of time and temperature are discussed, and a rationale is presented for the observed phenomena. There is a reasonable probability that the properties of the formic acid complex are due to strong interfacial polarization which is affected by the melting point at 120°C.

The Room Temperature Crystal Structure of 2-Ethylbenzimidazole

by

Che-Hsiung Hsu, M. H. Litt and H. W. Chen
J. Appl. Phys., in press.

The crystal and molecular structure of 2-ethylbenzimidazole has been determined by three dimensional single-crystal x-ray analysis. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 20.762(4)Å, b = 8.095(1)Å, c = 9.951(2)Å, and β = 100.06(2)°. Least-squares refinement of 696 reflections resulted in a final R factor of 0.072. There are two crystallographically independent molecules in the unit cell. The benzimidazole ring is planar. Molecules are linked together by NH ... N hydrogen bonds to form chains parallel to the c axis.